

# X-ray absorption and soft X-ray fluorescence analysis of KDP crystals

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## INTRODUCTION

Potassium Dihydrogen Phosphate (KDP) is a non-linear optical material used for laser frequency conversion. KDP optics undergo many stages of processing from raw single crystal substrates to functioning optical components. Their reliability is critical for the economic operation of future laser systems at LLNL. As part of the processing of KDP into optics, the material is diamond machined, annealed and then coated with a silica sol-gel. Previous investigations show that surface defects (etch pits) form when the KDP crystals are exposed to ambient humidity but are less susceptible to pitting following annealing in air (160°C, 7 days). Surface composition is never the same as bulk and annealing in air will certainly further affect this compositional difference. Understanding the surface chemistry may ultimately lead to a process to control the formation of these surface defects.

## EXPERIMENTAL

X-ray absorption spectroscopy (XAS) probes empty or unfilled electronic states and provides information on the local chemical environment. This analysis was performed at beamline 8.0.1 at the Advanced Light Source (ALS) by scanning the photon energy of the incoming monochromatic synchrotron radiation through the K 2p, P 2p (L<sub>2,3</sub>-edge) and O 1s (K-edge) core-level edges while monitoring the total electron yield (TEY, surface sensitive, 50-100Å) and fluorescence yield (FY, bulk sensitive, 0.1–1.0 µm).

Soft X-Ray fluorescence spectroscopy (SXRF) is a bulk-sensitive probe due to the long mean free path of photons in solids (0.1–1.0 µm). Since core levels are involved in absorption and emission, SXRF is both element- and angular-momentum-selective. SXRF measures the local element specific partial density of states (DOS).

In SXRF, a valence emission spectrum results from transitions from valence band states to the core hole produced by the incident photons. In the non-resonant energy regime, the excitation energy is far above the core binding energy, and the absorption and emission events are uncoupled. The fluorescence spectrum resembles emission spectra acquired using energetic electrons and is insensitive to the incident photon's energy. In the resonant excitation energy regime, core electrons are excited by photons to unoccupied states just above the Fermi level. The absorption and emission events are coupled and this coupling manifests itself in several ways depending in part on the localization of the empty electronic states in the material.

## RESULTS

The O K-edge XANES spectra presented in Figure 1 reveal distinct chemical differences between unannealed and annealed KDP. The differences between the TEY (surface sensitive) and FY (bulk sensitive) spectra for each sample suggests differences in surface versus bulk composition. The excitonic peak at ≈538 eV is usually attributed to double bonded oxygen. In addition, the spectral differences observed in the σ bonded O peak indicate that the O atom is coordinated by a different number and type of ligand in the unannealed versus annealed material. [1,2]

The SXRF spectra associated with the O K-edge XANES also reveal compositional differences between the bulk unannealed and annealed KDP. The SXRF spectra were acquired at the energy positions indicated on the XANES spectra. Momentum conservation and selectivity are very much in force for all the excitation energies above, equal to, and below the π\* energy at

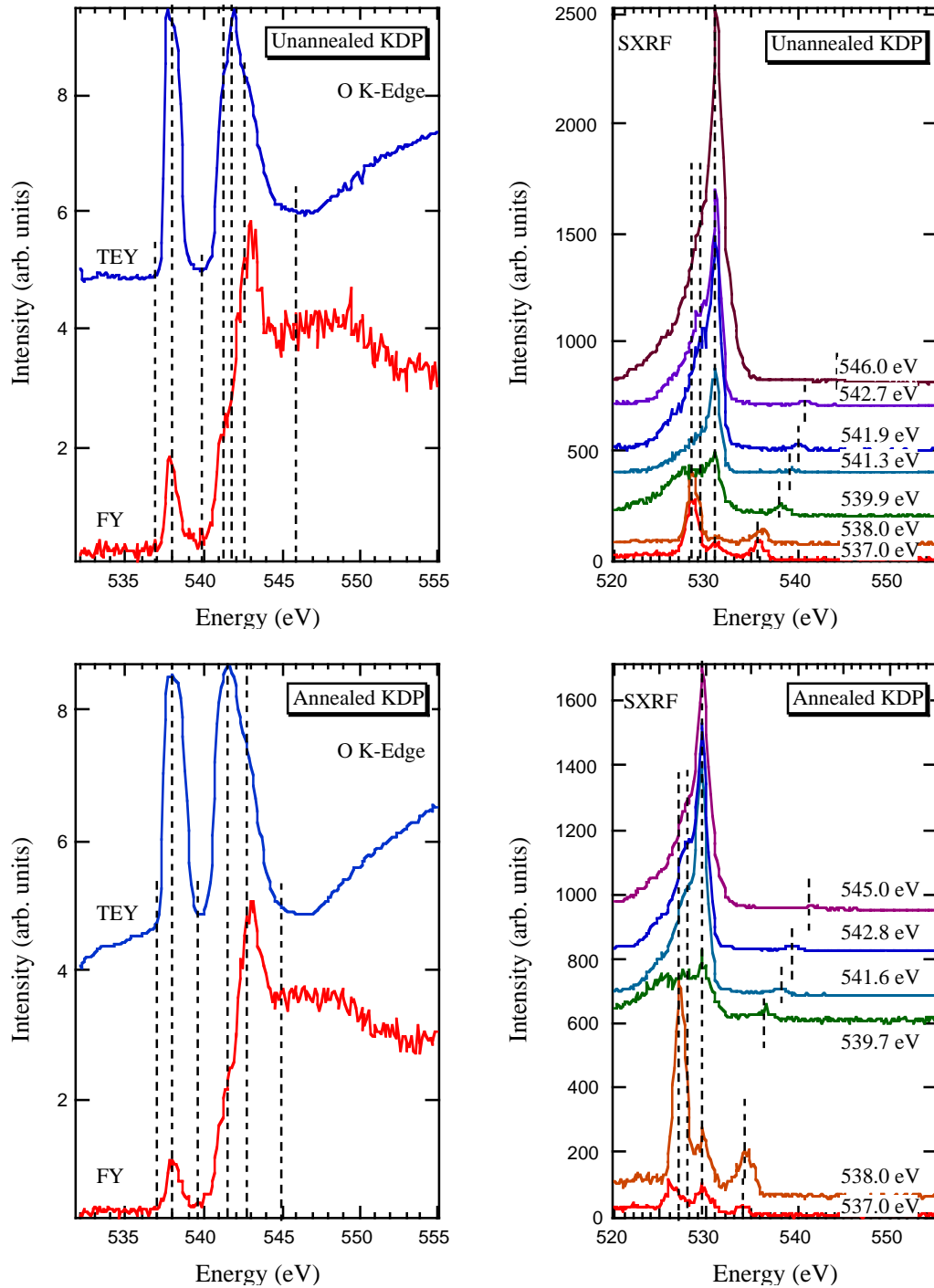


Figure 1. O K-edge XAS and SXRF spectra of unannealed and annealed diamond turned KDP.

$\approx 538$  eV. Below this feature, three peaks are observed in the SXRF spectra for the unannealed material. The same three peaks have different intensity ratios in the SXRF spectra for the annealed material, again indicating a change in composition and structure due to annealing in air. In addition, the peak at  $h\nu' \approx 528$  eV decreases in intensity as we move through the  $\pi^*$  energy and then reappears and slightly shifted to higher energy. At the  $\sigma^*$  edge, the feature located at  $h\nu' \approx 531$  eV does not move with excitation energy. Note that its increased intensity corresponds with the  $\sigma^*$  absorption edge energy ( $h\nu = 541.3$  eV). The other dispersive feature at higher energy may also be associated with valence band electronic structure.

Comparing the P  $L_{2,3}$ -edge XANES spectra presented in Figure 2, the peak structure is different for the unannealed versus annealed KDP. The spectral structure for the unannealed KDP is indicative of a pyrophosphate phase by comparison with literature spectra.[1,2] Similarly, the spectral structure for the annealed KDP is indicative of an orthophosphate phase. Specifically, the development of the feature at 133.6 eV in our annealed spectrum is similar to a feature seen in the literature spectrum for an orthophosphate. In addition, the intensity ratios of the features at 133.6 eV and 134.5 eV changes after annealing, also observed in the literature spectrum for an orthophosphate.

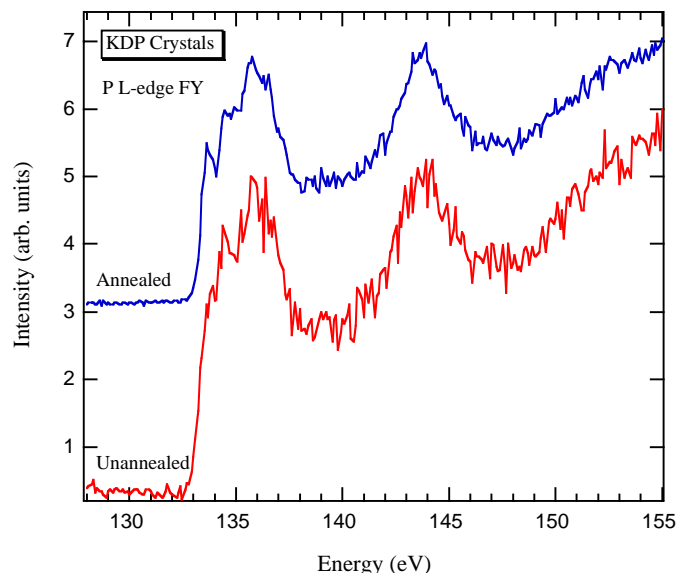


Figure 2. Phosphorus L-edge XANES spectra of unannealed and annealed diamond turned KDP measured in fluorescence yield mode.

## SUMMARY

X-Ray absorption and soft X-Ray fluorescence spectroscopies were used to characterize the chemical and electronic structure of diamond-turned potassium dihydrogen phosphate (KDP) crystals before and after annealing. Distinct spectroscopic differences in the P and O spectra were observed between the unannealed and annealed KDP. Results indicate that the unannealed surface may be a pyrophosphate, not stoichiometric KDP. Results also indicate that the annealed surface may have been converted to an orthophosphate. This preliminary work represents the first evidence that the surface structure of the KDP changes during the annealing process. We will continue this work in an effort to understand how the change in the KDP surface structure affects etch pit formation.

## REFERENCES

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